



Transport of Nanoparticles of Zerovalent Copper, Zinc Oxide, and Titanium Dioxide in Saturated Porous Media

57th Annual Oklahoma ACS Pentasectional Meeting
March 17, 2012, Lawton, Oklahoma

Chunming Su, EPA
Edward H. Jones, NRC
Gixin Chen, NRC
Xuyang Liu, NRC

United States Environmental Protection Agency (EPA)
and National Research Council (NRC) Resident Research
Associateship Program

Office of Research and Development
National Risk Management Research Laboratory
Ground Water and Ecosystems Restoration Division, Ada, OK

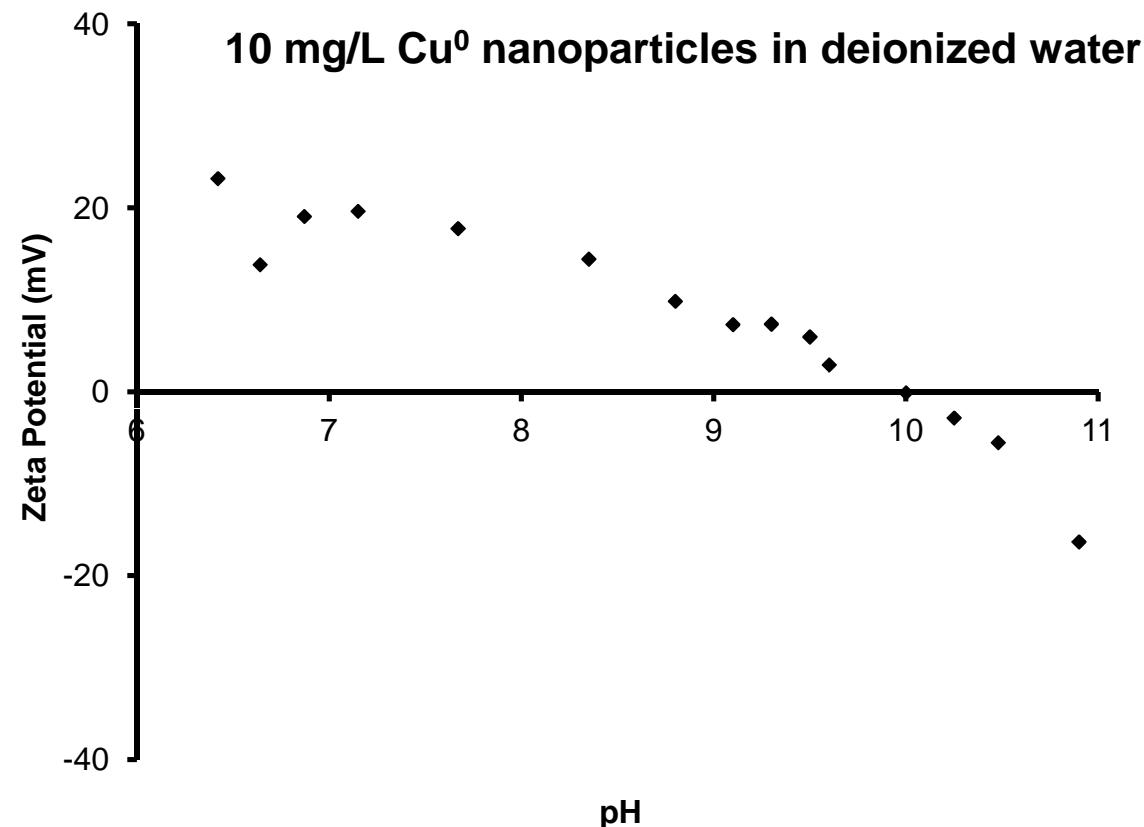
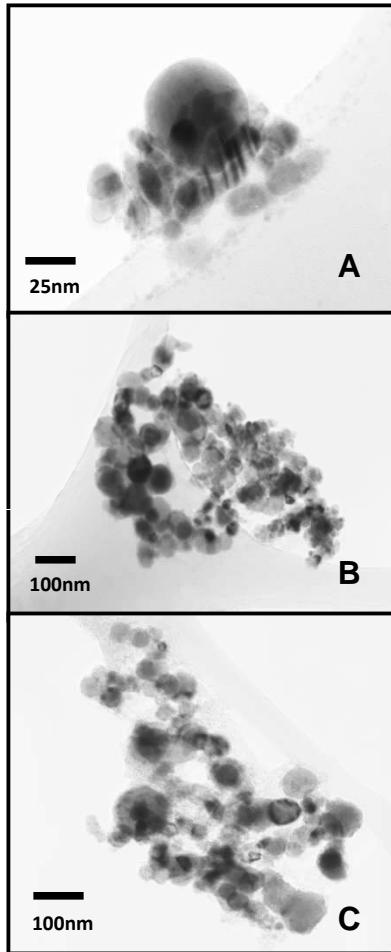
Introduction

- Nanomaterials are being manufactured and utilized at increasing rates
- Little is known about their fate and transport in the subsurface
- Consequently it is difficult to evaluate exposure risks, conduct life cycle analysis, and develop waste management strategies
- The overall goal of this research is to investigate the mechanisms governing the transport and deposition of nanomaterial aggregates in saturated porous media and to identify factors causing the deviation of the transport behavior from traditional filtration theory predictions

Experimental Work

- Zeta Potential and Particle Size Distributions
- SEM and TEM images
- Column Tests
 - Different Porous Media (Sand) Characteristics
 - Experimental Flow Rates
 - Geochemical Characteristics
 - Nanoparticles (from Nanostructured & Amorphous Materials Inc.):
 - Elemental Copper
 - Zinc Oxide
 - Titanium Dioxide

Zeta Potential and pH: Cu⁰ Nanoparticles

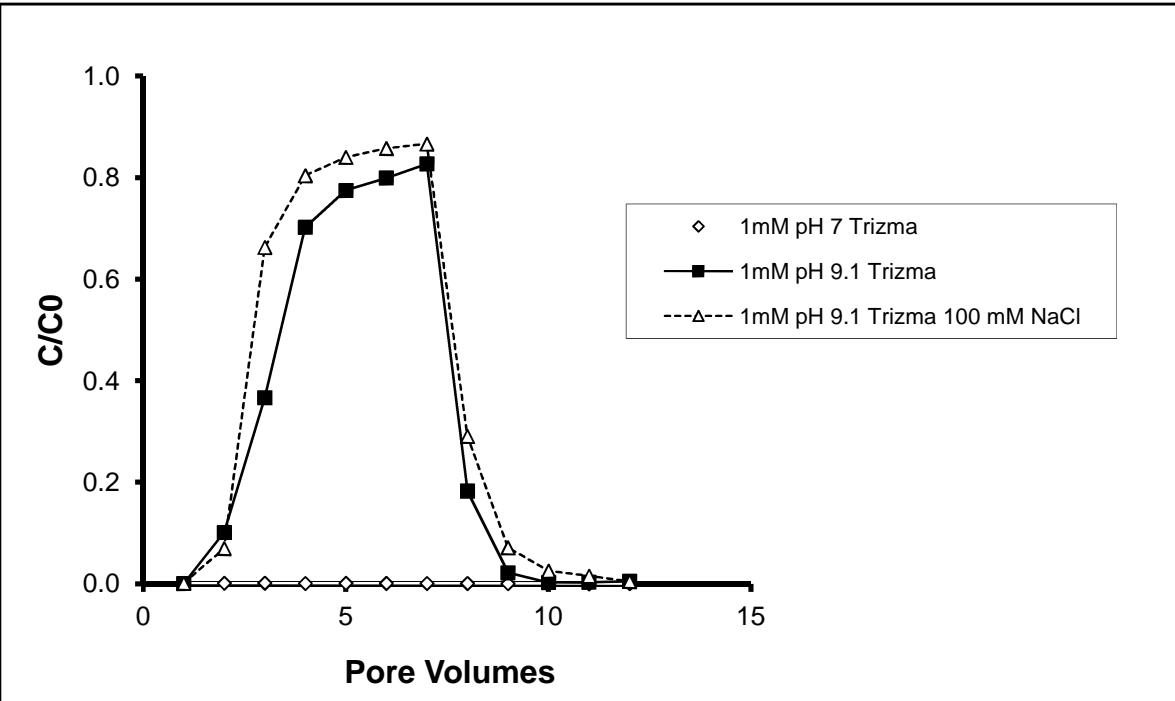


A: Individual Cu⁰ nanoparticles (10 to 50 nm, nominal size 25 nm from vendor)

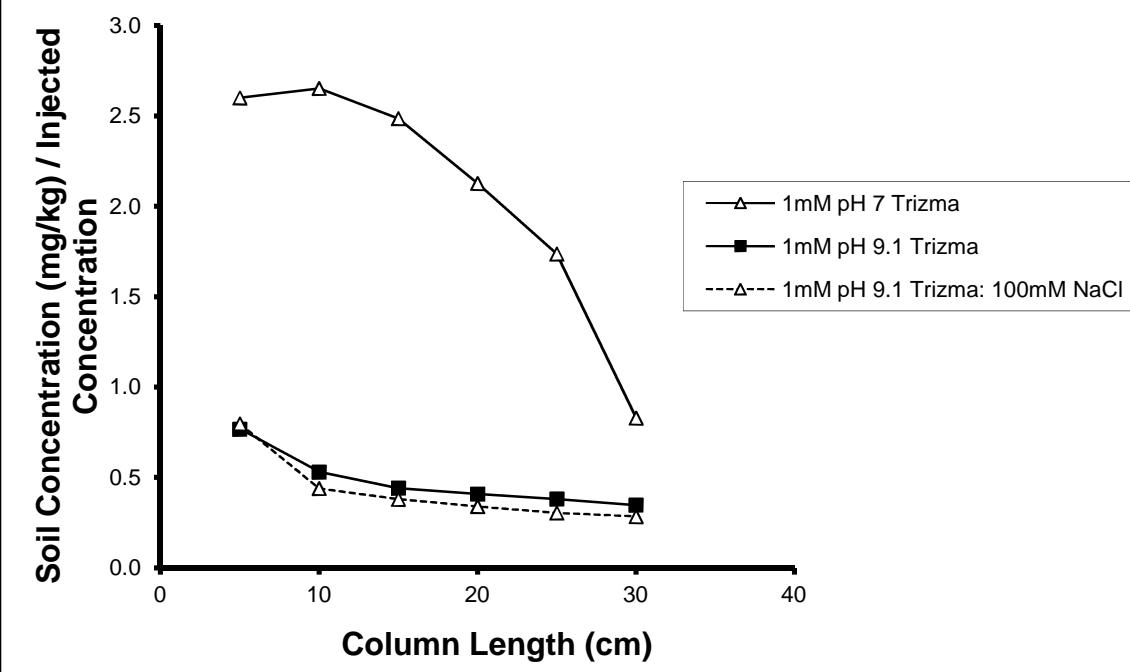
B: Small Cu⁰ nanoparticle aggregates

C: Large Cu⁰ nanoparticle aggregates

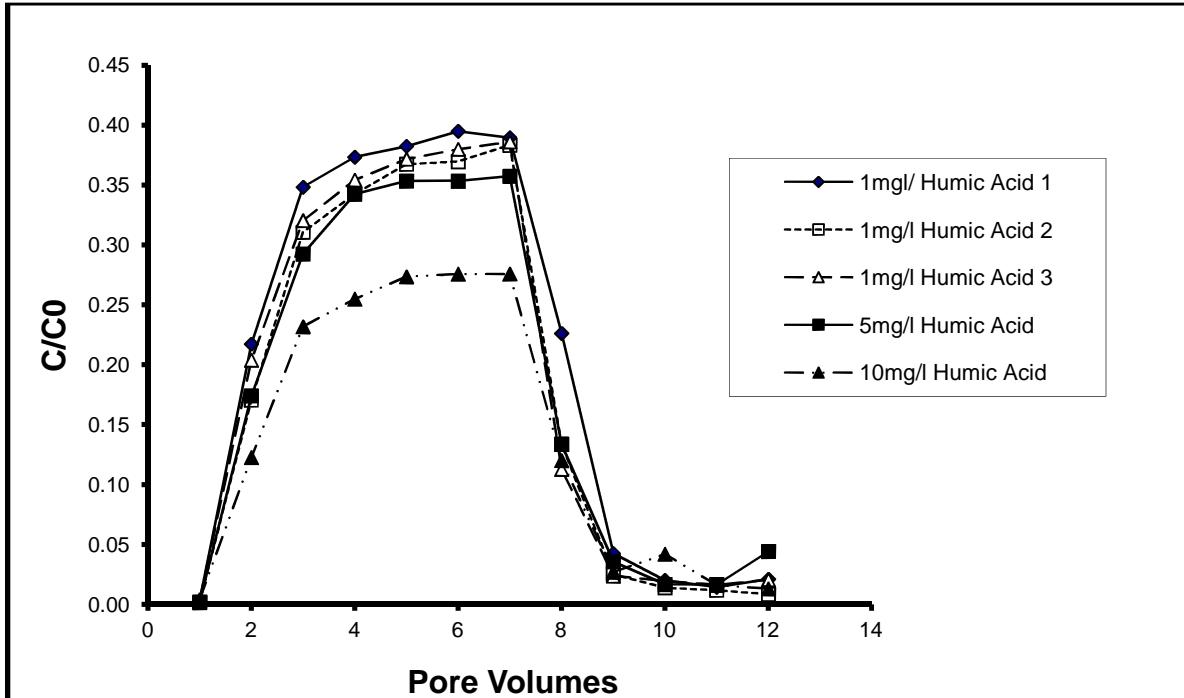
Effluent Breakthrough Curve for Cu⁰



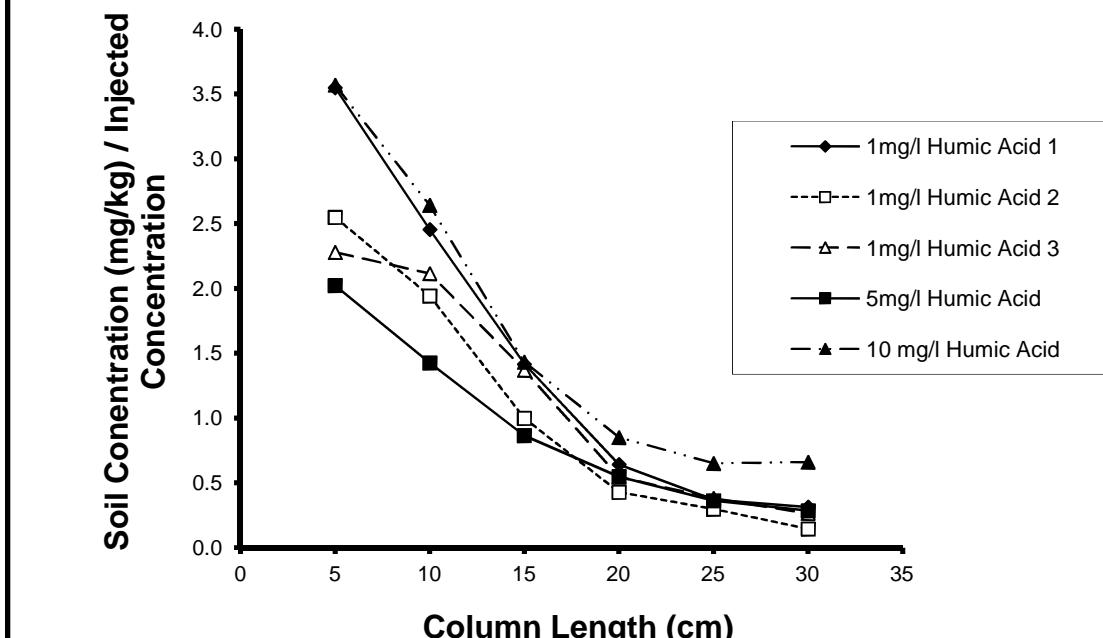
Retention Profile



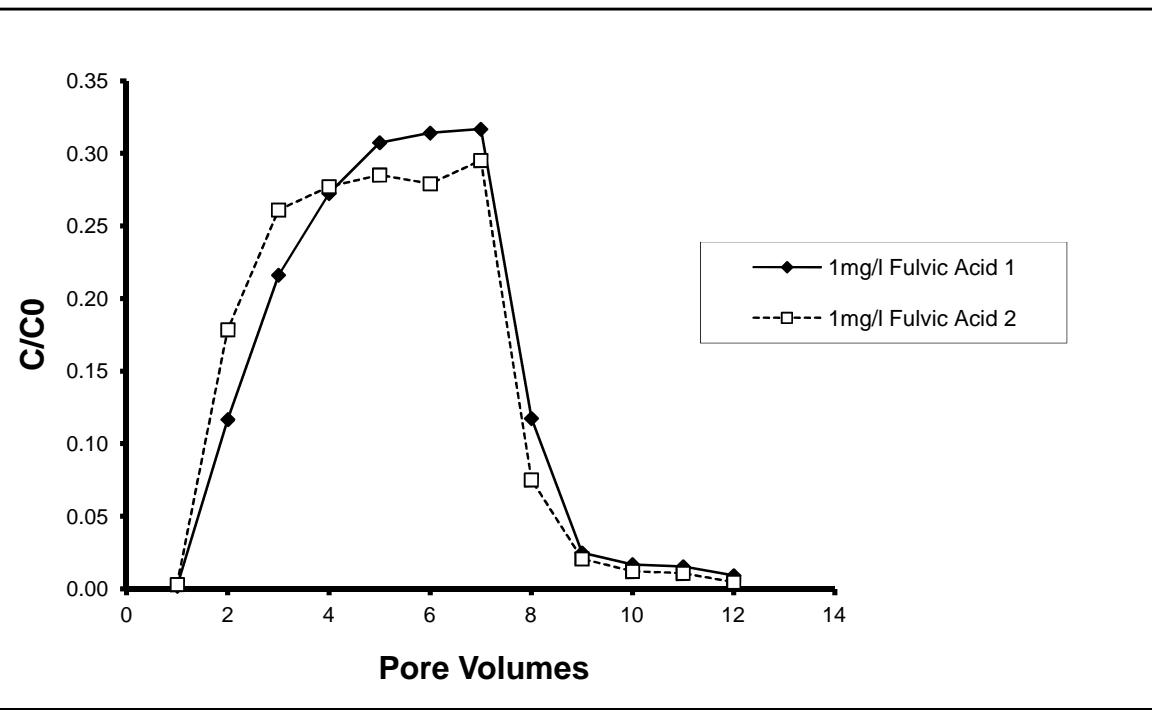
Effluent Breakthrough Curve for Cu⁰



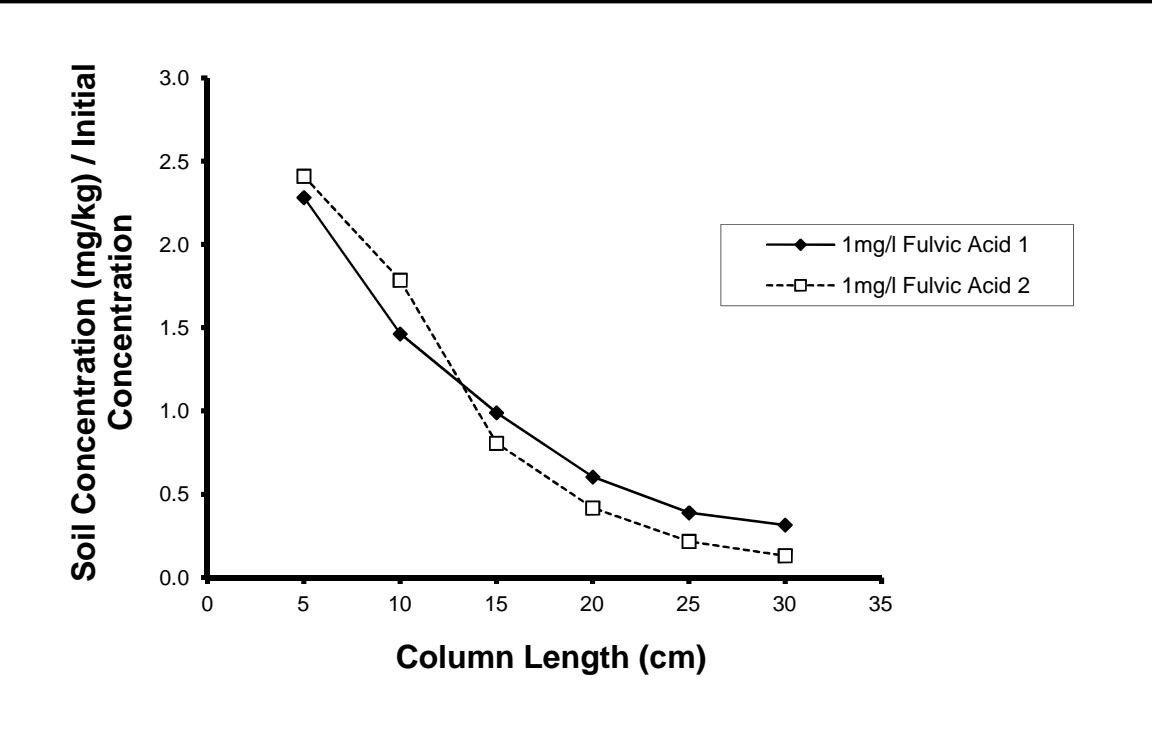
Retention Profile



Effluent Breakthrough Curve for Cu⁰



Retention Profile

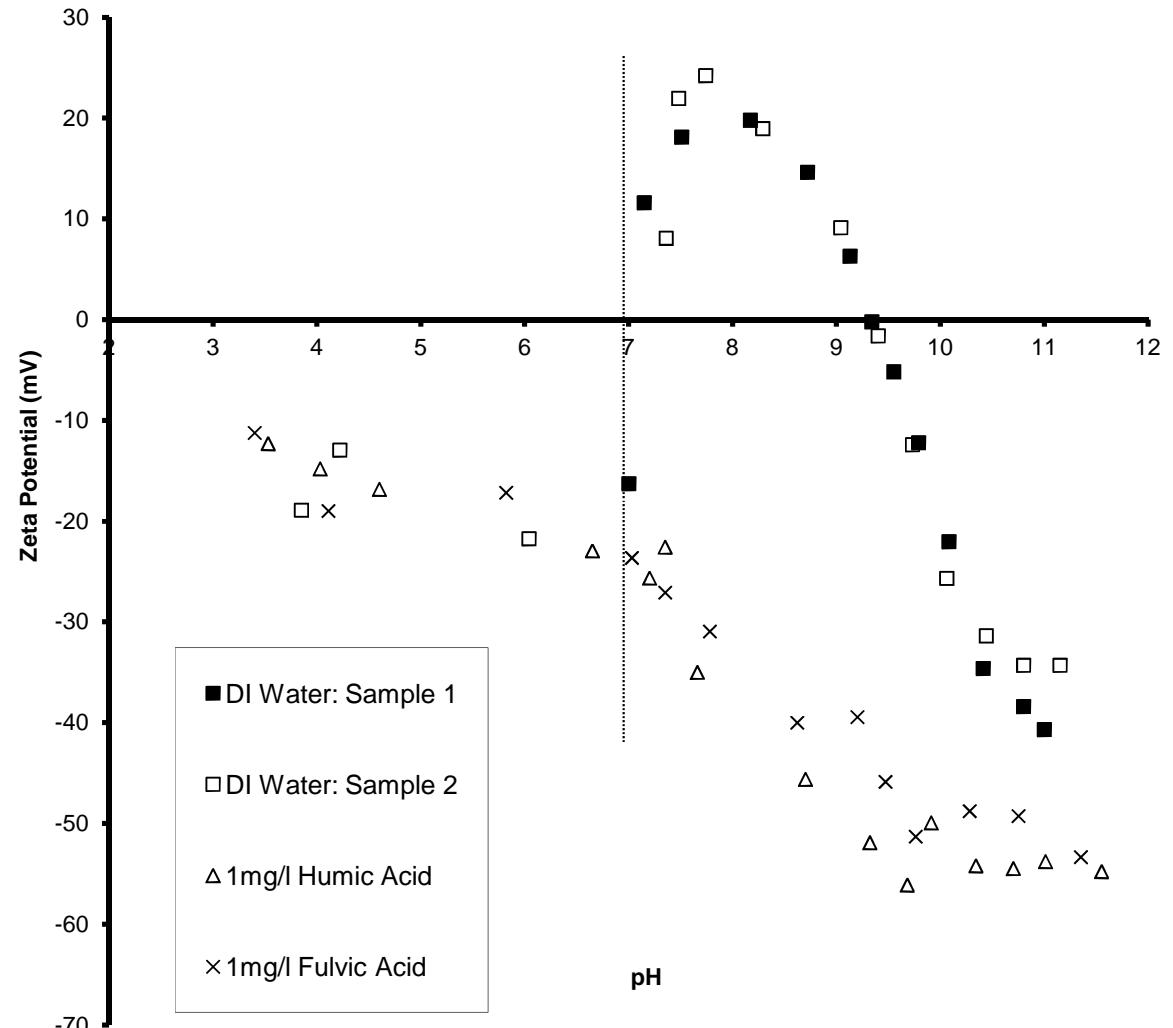
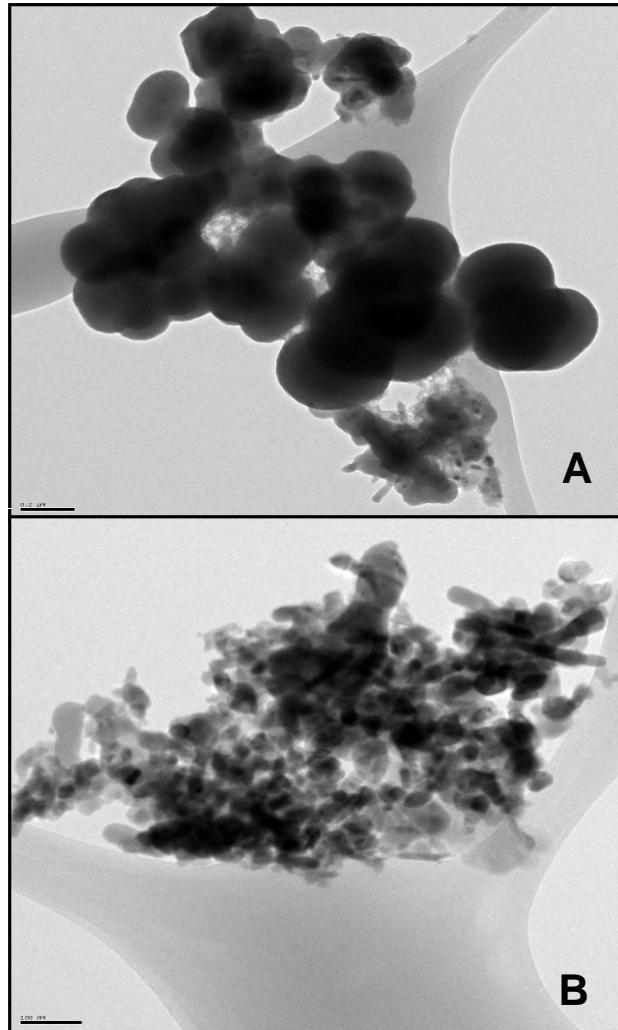


Summary

- Bare Cu⁰ nanoparticles were not transported through the porous media used in this study
- Presence of NOM and an organic buffer dramatically improved Cu⁰ transport and was attributed to electrostatic and electrosteric stabilization of the nanoparticles
- However, the attachment efficiency factor (α) values calculated from retention profile and effluent BTCs disagree. This discrepancy would indicate that the transport of Cu⁰ nanoparticles doesn't follow traditional CFT as it does not include these additional mechanisms such as surface roughness, surface charge, and population heterogeneity
- Journal Publication

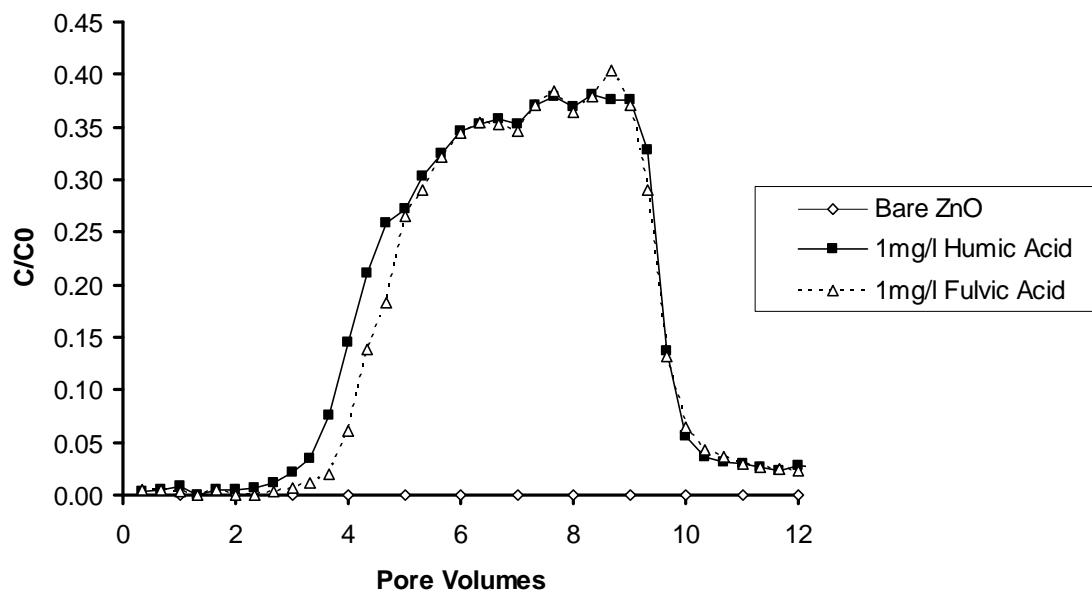
Jones, E.H. and Su, C. (2011) Fate and transport of elemental copper (Cu⁰) nanoparticles through saturated porous media in the presence of organic materials. Water Research, 46: 2445-2456.

Zeta Potential and pH: ZnO Nanoparticles

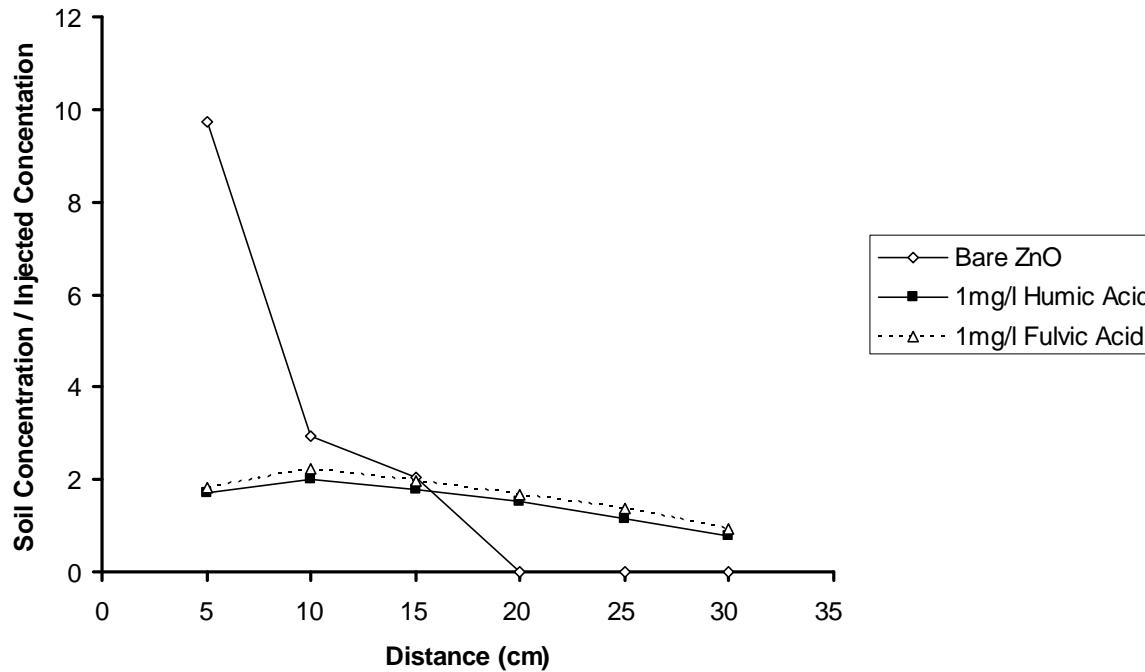


PZC in DI water = 9.2, charge reversal at pH 7.0

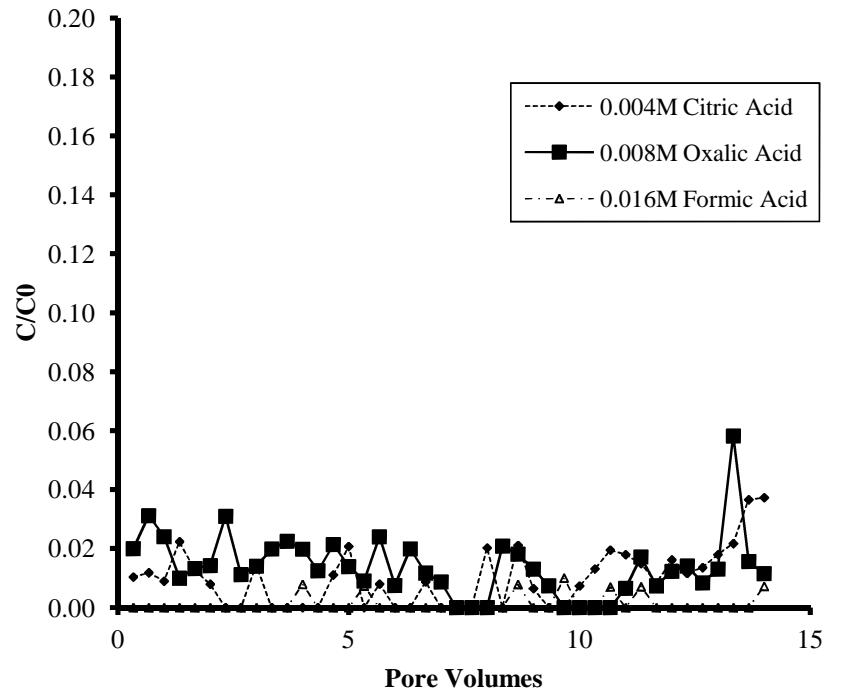
Effluent Breakthrough Curve for ZnO



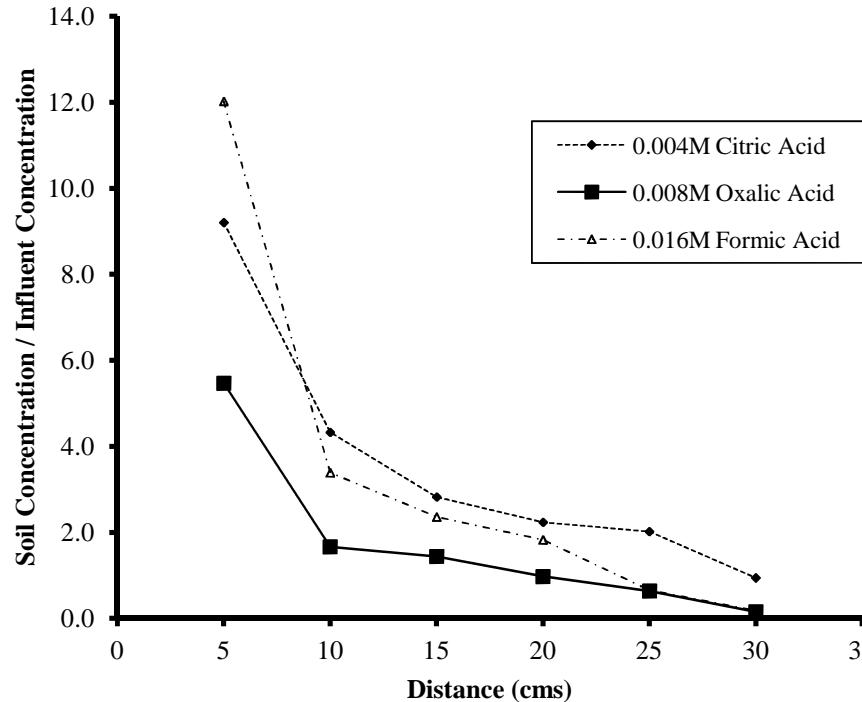
Retention Profile



Effluent Breakthrough Curve for ZnO



Retention Profile

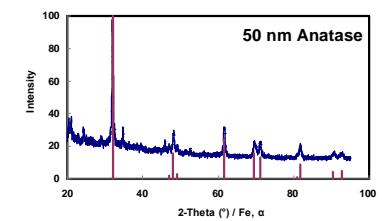
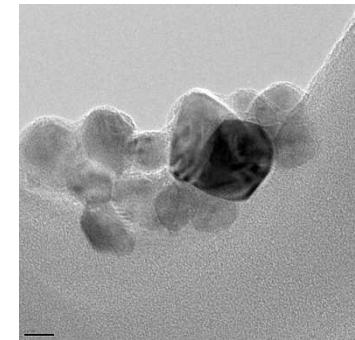
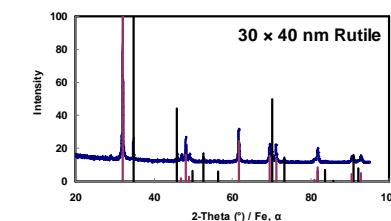
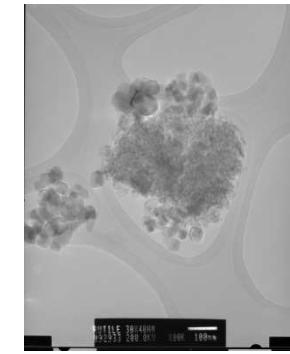
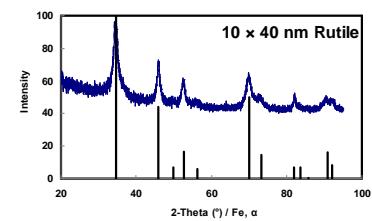
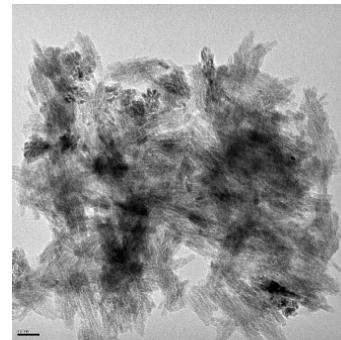
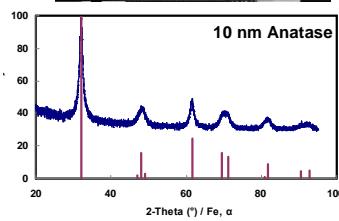
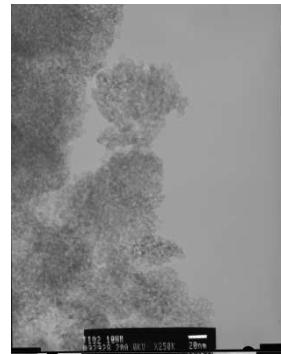
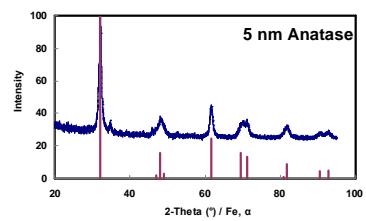
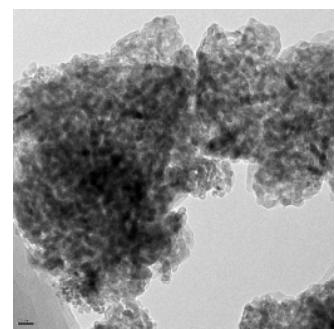


Summary

- Bare ZnO nanoparticles exhibited negligible mobility through porous media
 - Presence of natural organic matter dramatically improved ZnO transport and was attributed to electrostatic and electrosteric stabilization of the nanoparticles by organic matter
 - However, the attachment efficiency factor (α) values calculated from retention profile and effluent BTCs disagree. This discrepancy would indicate that the transport of ZnO nanoparticles doesn't follow traditional CFT as it does not include these additional mechanisms such as surface roughness, surface charge, and population heterogeneity
 - Journal Publication

Jones, E.H. and Su, C. (2012) Transport and retention of zinc oxide nanoparticles in porous media in the presence of natural organic ligands (In preparation)

Characterization of five types of TiO_2 NPs



5 nm anatase

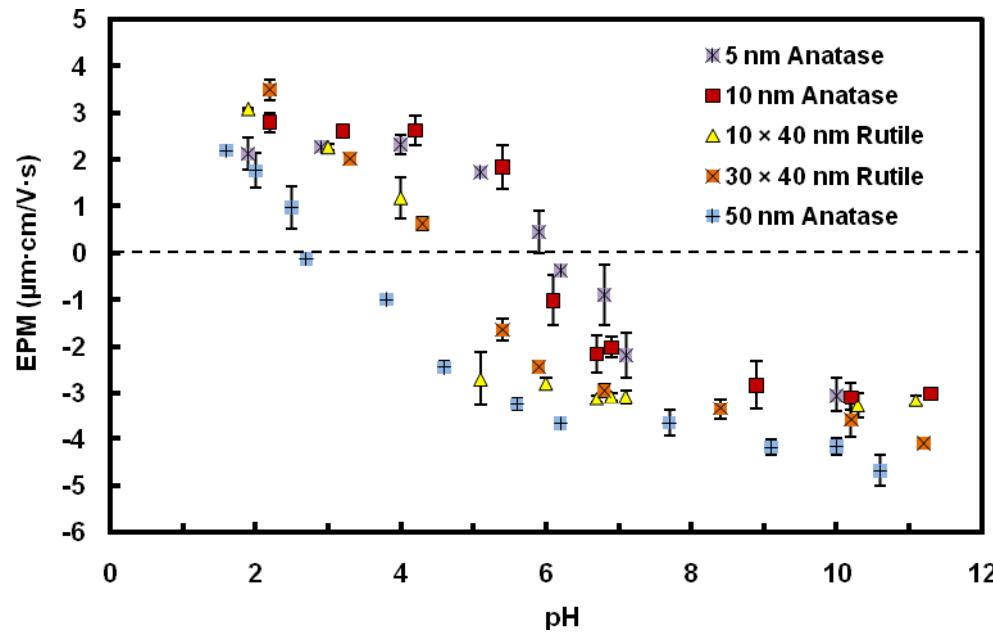
10 nm antase

10×40 nm
rutile

30×40 nm "rutile" -
lesser anatase
found.

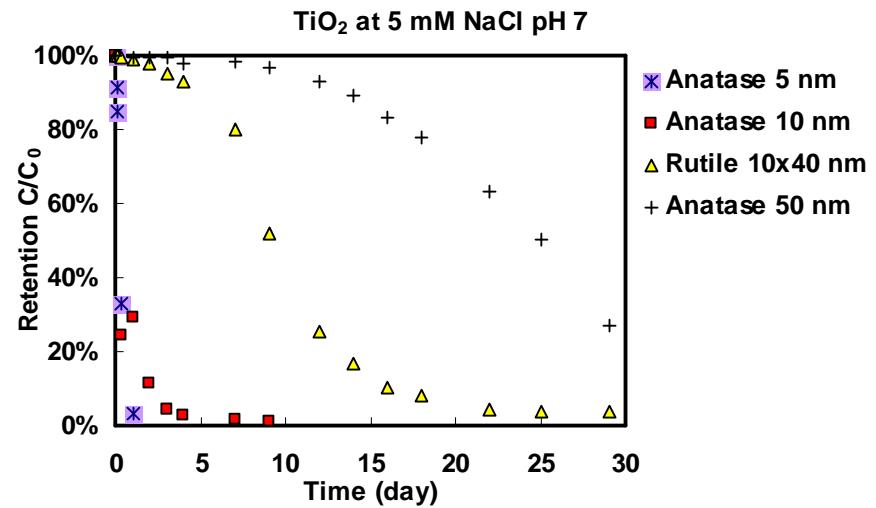
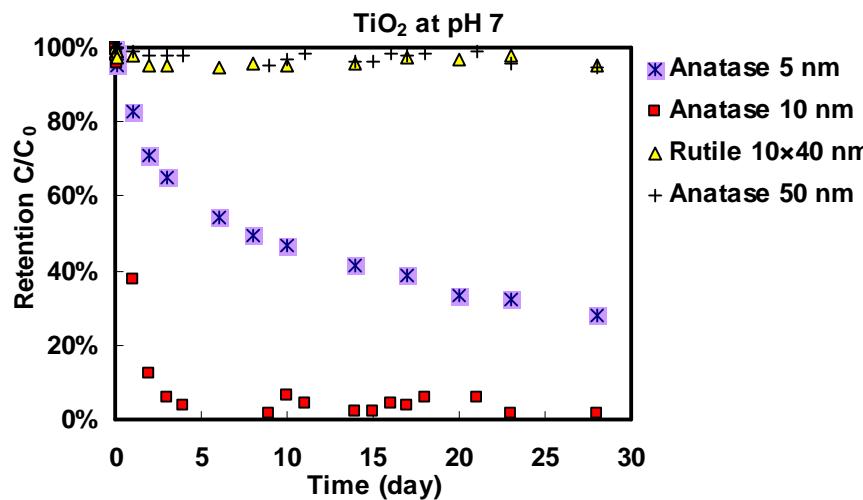
50 nm
anatase

Electrophoretic Mobility (EPM) of TiO₂ NPs



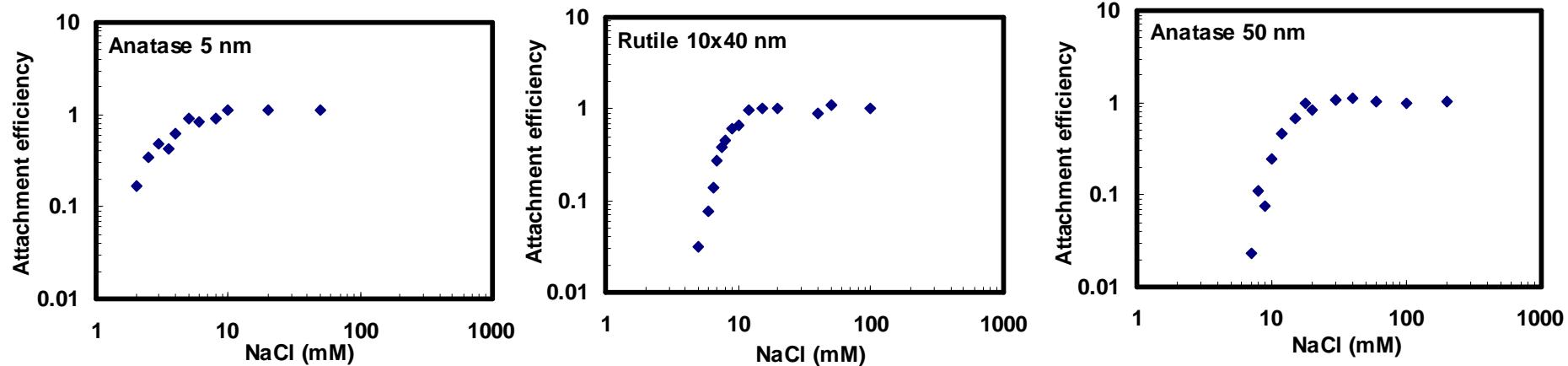
	Anatase 5 nm	Anatase 10 nm	Rutile 10×40 nm	Rutile 30×40 nm	Anatase 50 nm
EPM at unadjusted pH (pH 4.7), ($\mu\text{mCm/Vs}$)	1.729	1.841	-2.71	0.625	-2.449
PZC	6	6	4.4	4.7	2.7

Sedimentation of TiO_2 NPs



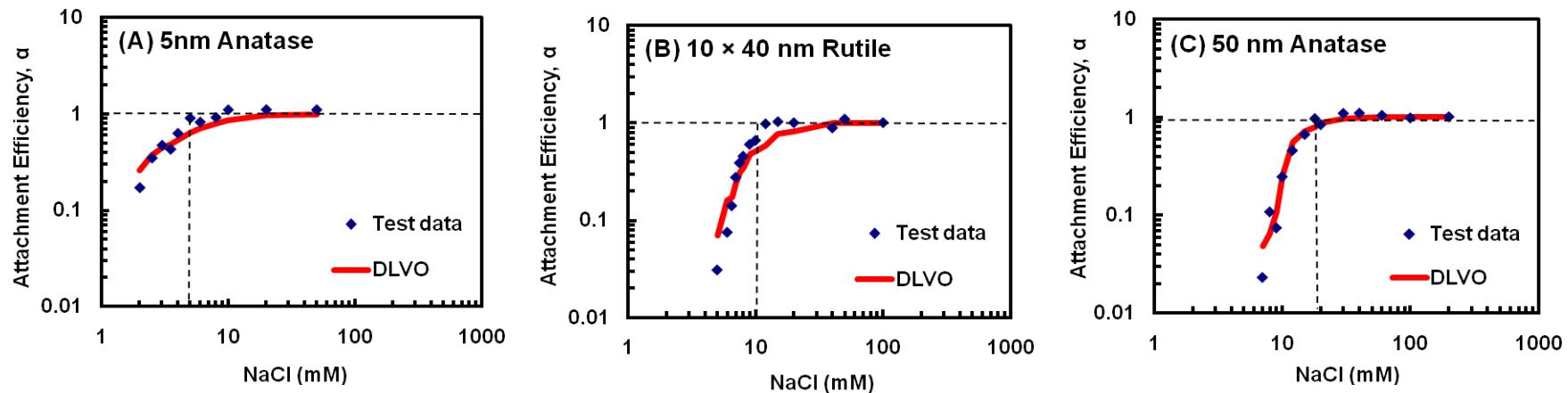
EPM ($\mu\text{mCm/Vs}$)	Anatase 5 nm	Anatase 10 nm	Rutile 10x40 nm	Anatase 50 nm
pH 7 in DI Water	-2.19	-2.02	-3.09	-3.67
pH 7 at 5 mM NaCl	-1.18	-1.28	-2.64	-3.29

Aggregation Kinetics Experiment



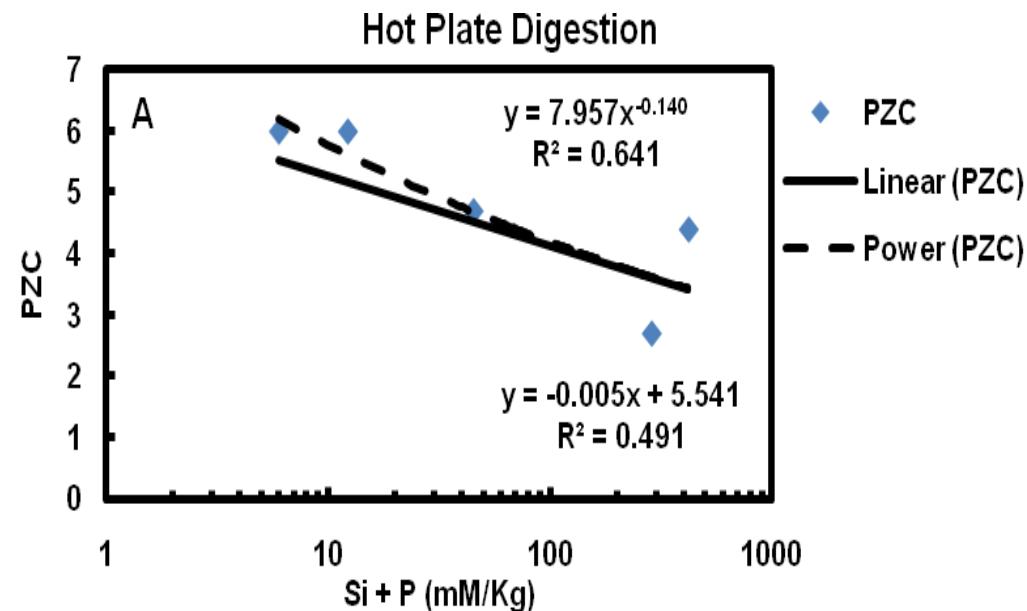
- Both reaction controlled regime and diffusion controlled regime for all TiO_2 NPs.
- The CCC of NaCl for 5 nm anatase, 10×40 nm rutile and 50 nm anatase were 5 mM, 10 mM and 18 mM
- In concurrence with the sediment test conducted.

Prediction by DLVO Model



- Data can be fit reasonably well with the DLVO theory.
- Derjaguin Approximation (DA).
 - For 50 nm anatase, $R/\kappa^{-1} > 10$ (at $\text{NaCl} > 15 \text{ mM}$).
- Other factors, e.g. surface heterogeneities, roughness.
- $H_{W-\text{TiO}_2-W}$: $7.0 \times 10^{-20} \text{ J}$, $5.9 \times 10^{-20} \text{ J}$ and $5.8 \times 10^{-20} \text{ J}$.

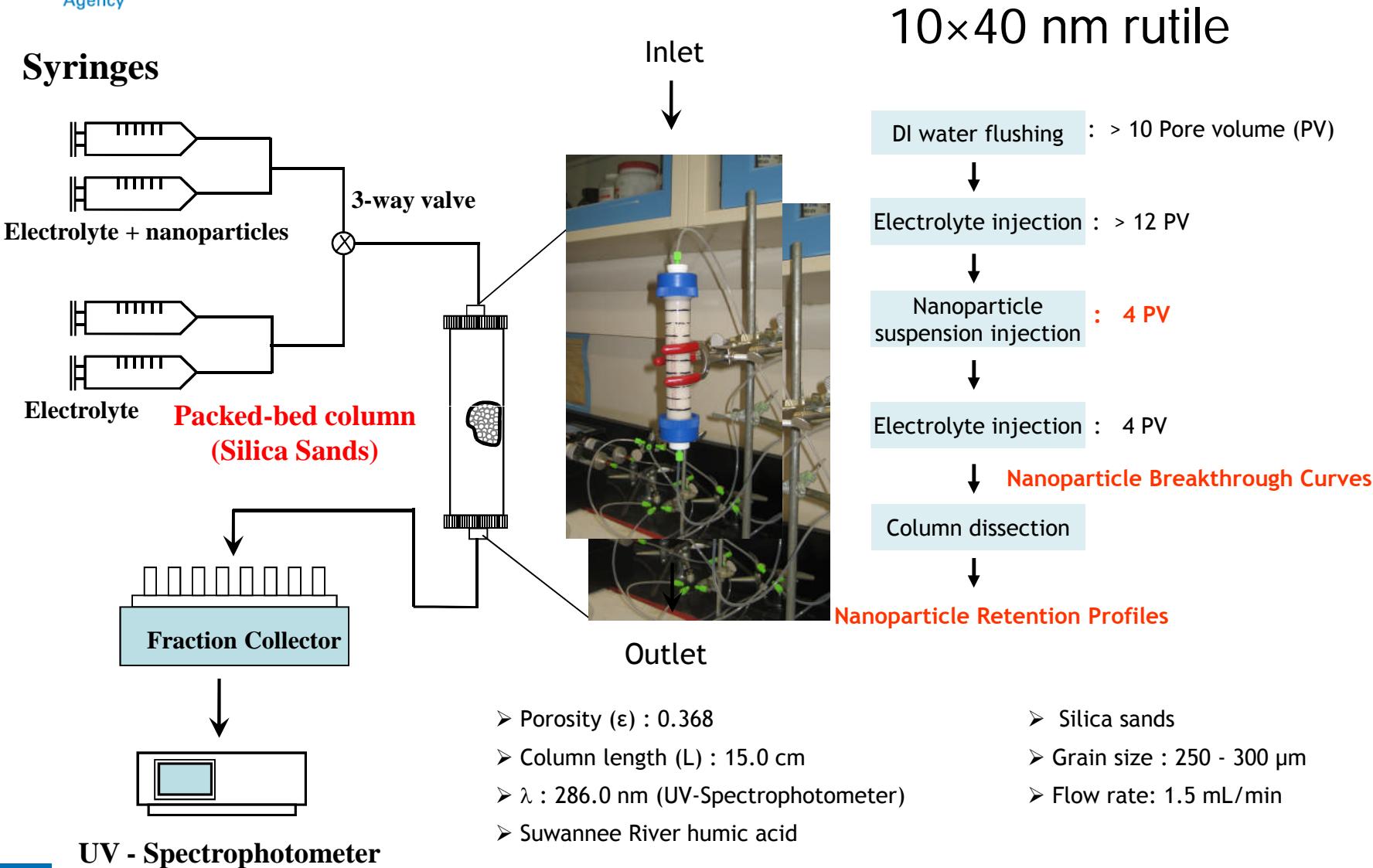
Effect of Composition on EPM



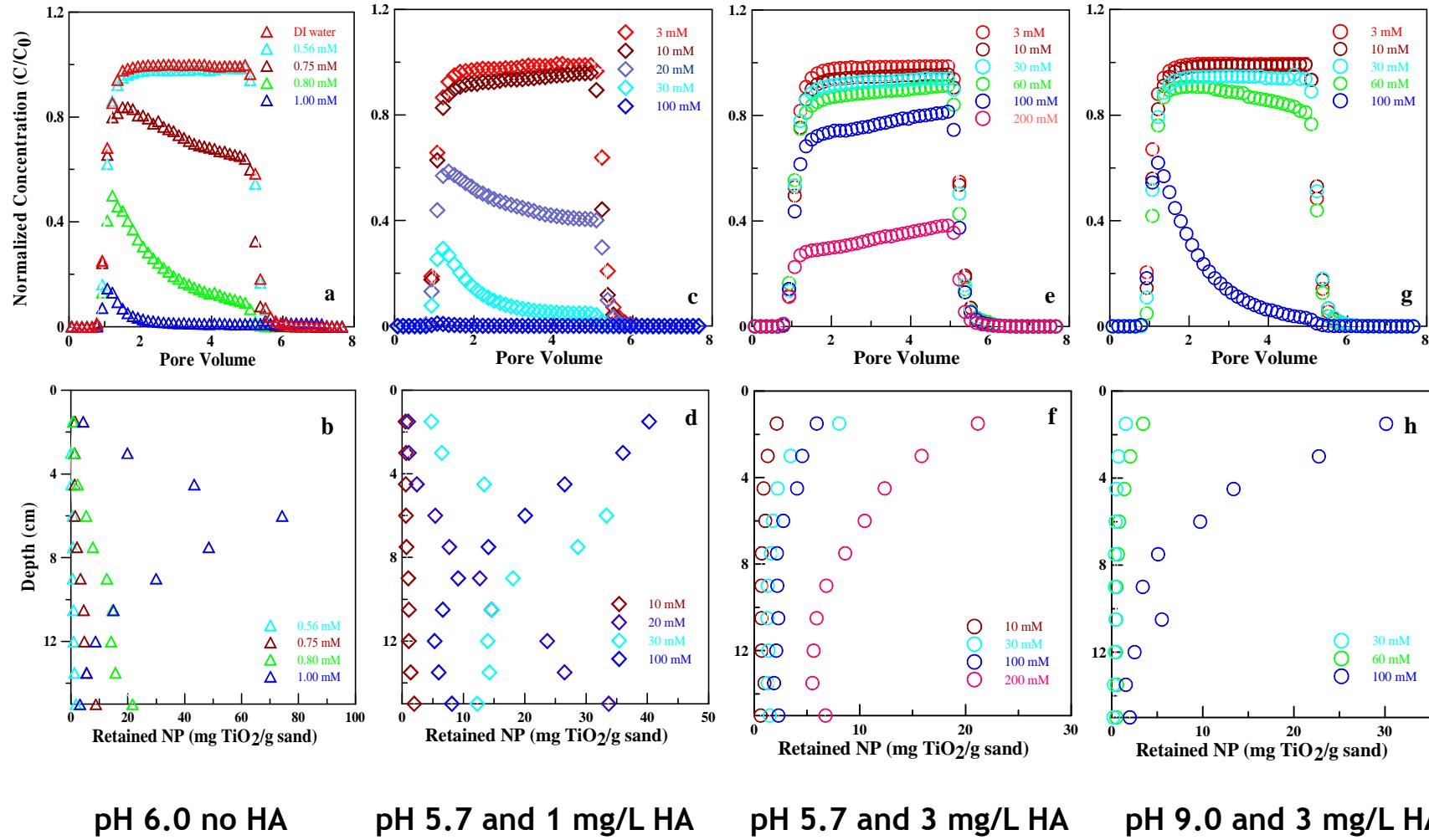
- The PZC can be correlated quantitatively with the amounts of extractable impurities (i.e. Si, P) in the pristine TiO_2 nanomaterials.
 - PZC decreased with the increase in extractable silicon and phosphorus contents in a linear or power trend.

Liu, X; Chen, G; Su, C. 2011. Effects of material properties on sedimentation and aggregation of titanium dioxide nanoparticles of anatase and rutile in the aqueous phase. *J. Colloid Interface Sci.* 363, 89-93.

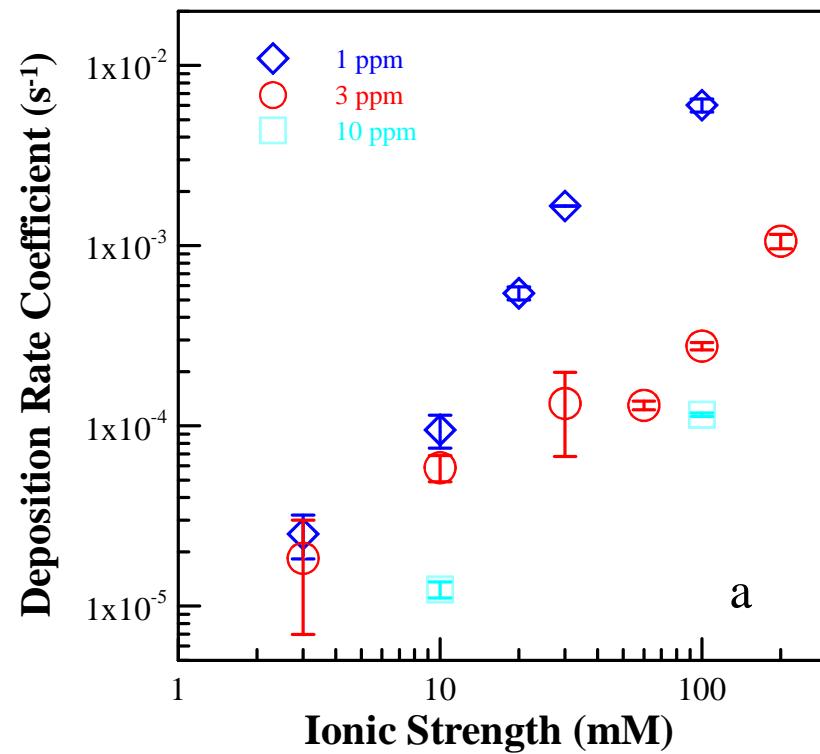
TiO₂ Transport Experiment Setup



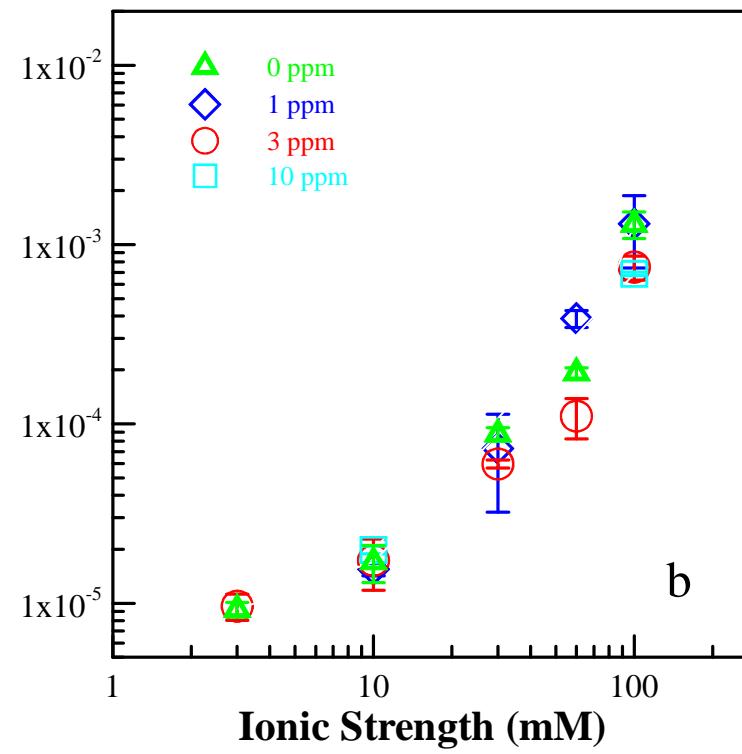
Representative Breakthrough Curves and Retention Profiles



Apparent Deposition Rate Coefficient



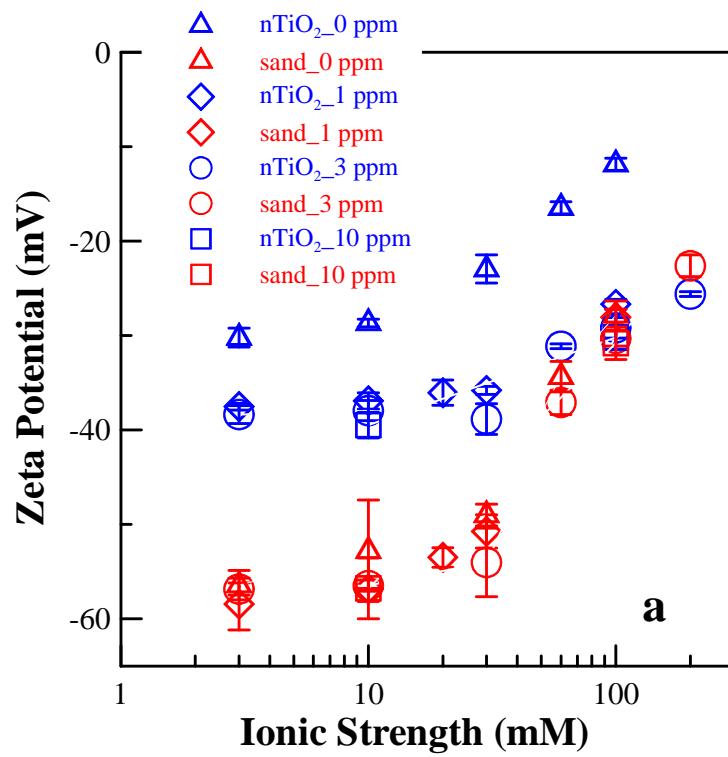
pH 5.7



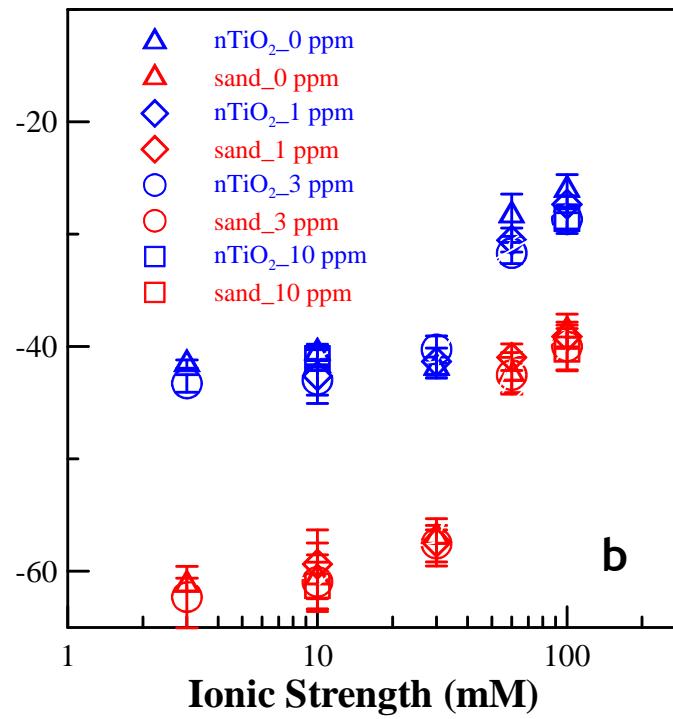
pH 9.0

$$k_d = -\frac{U}{\epsilon L} \ln\left(\frac{C}{C_0}\right)$$

Zeta Potential Measurements

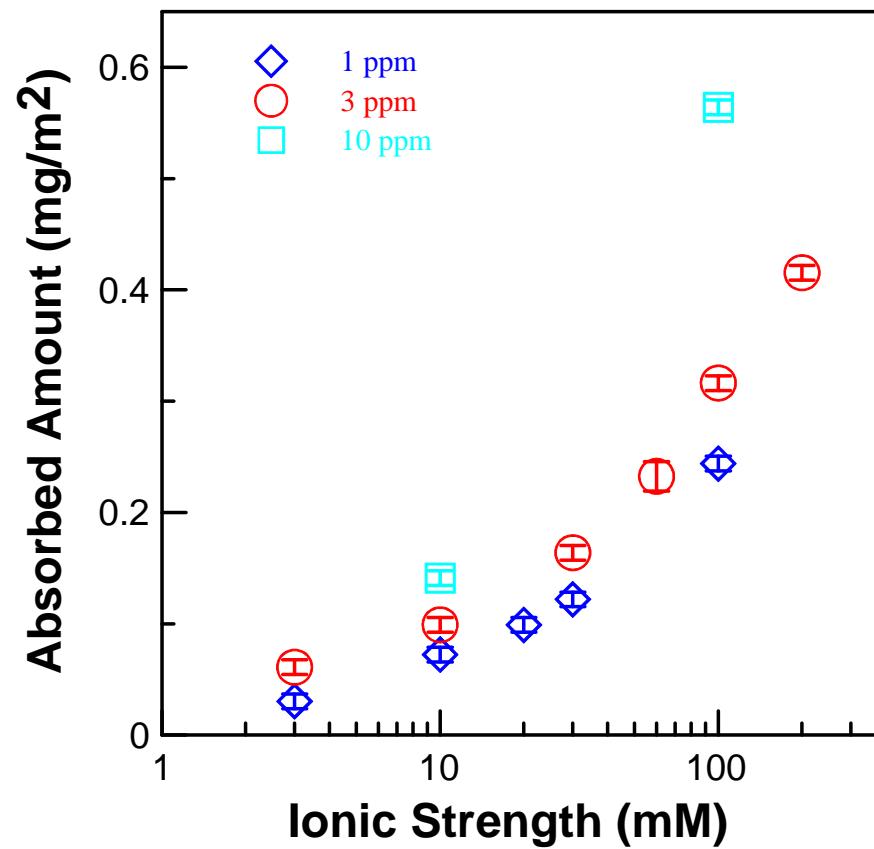


pH 5.7



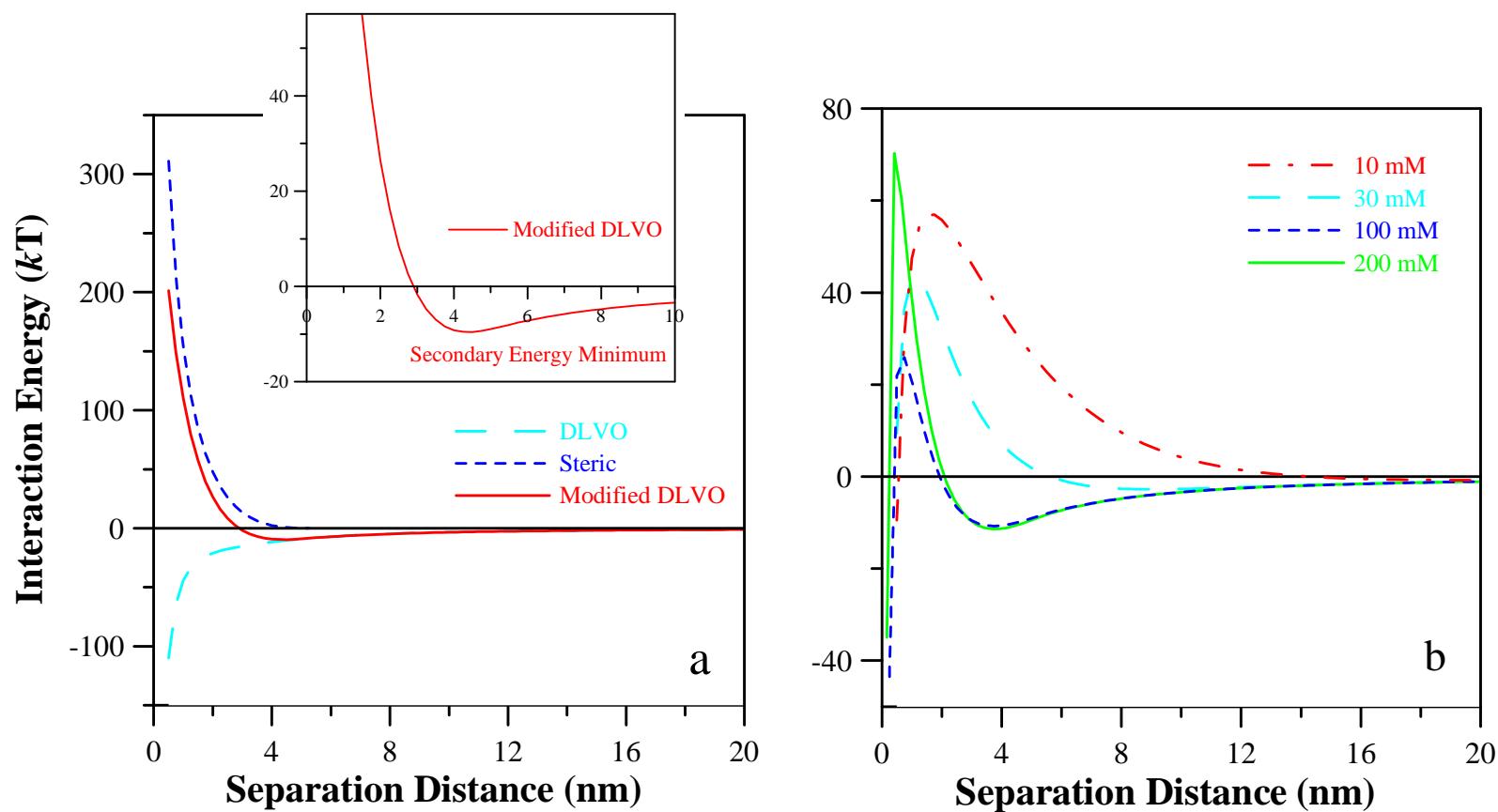
pH 9.0

Adsorption of HA on nTiO₂



pH 5.7

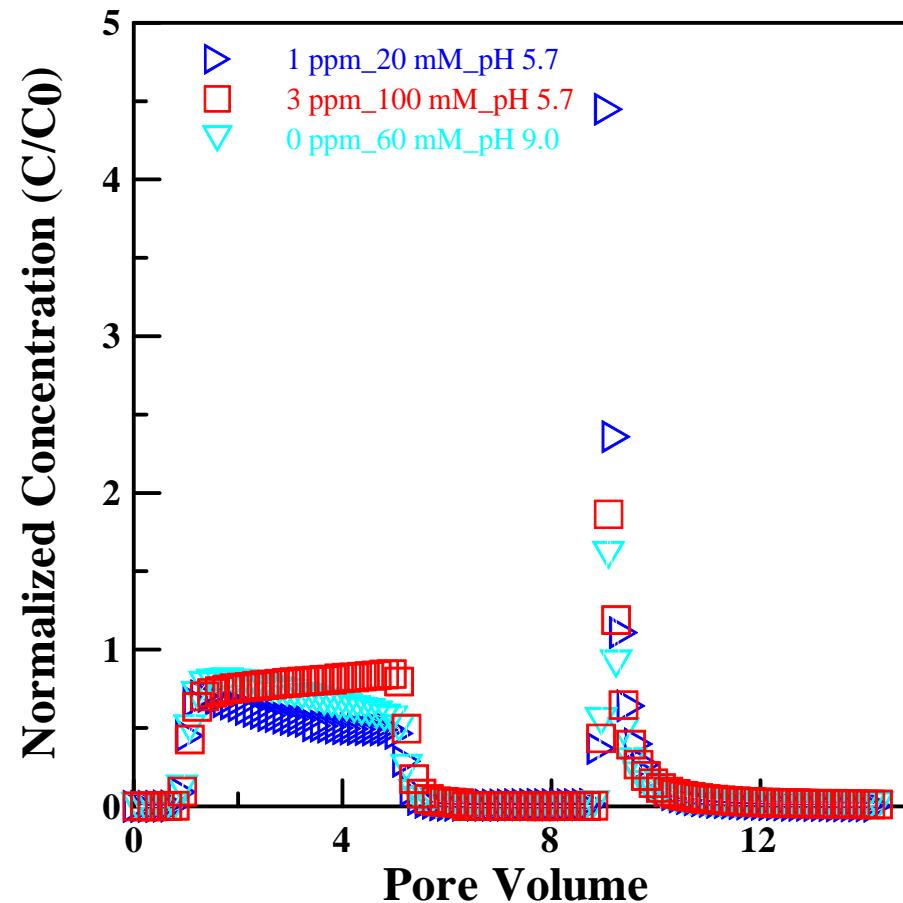
Modified DLVO Interaction Calculations



100 mM, 10 ppm HA and pH 5.7

3 ppm HA and pH 5.7

Experimental Evidence of Secondary Energy Minimum



Chen, G; Liu, X; Su, C. 2011. Transport and retention of TiO₂ rutile nanoparticles in saturated porous media under low-ionic-strength conditions: Measurements and Mechanisms. Langmuir 27, 5393-5402.

Summary

- Natural organic matter greatly enhanced nTiO₂ mobility at pH 5.7 through
 - increasing the negative surface charge of nTiO₂ at low HA adsorption densities
 - increasing electrostatic and steric interactions at high HA adsorption densities
- No significant impact of NOM on nTiO₂ mobility at pH 9.0 was observed
- The secondary energy minimum played an important role to retain nTiO₂ in porous media at the conditions studied
- NOM and solution pH are likely key factors that govern the stability and mobility of nTiO₂ in the natural aquatic environment
- Previously reported mobility of nTiO₂ at acidic background solution conditions which often overlooked the impact of NOM thus may lead to an underestimation of the potential transportability of nTiO₂ in real aquatic environments

Questions?

